

1 DEGRADABLE CHEMILUMINESCENT PROCESS AND PRODUCT

2
3 FIELD OF THE INVENTION

4 This invention relates to chemiluminescent processes and
5 products; particularly to a chemiluminescent article of
6 manufacture and chemical system which are biodegradable
7 subsequent to their use; and most particularly to a product
8 capable of losing its physical form and re-entering the
9 environment.

10
11 BACKGROUND OF THE INVENTION

12 Chemiluminescence relates to the production of visible
13 light attributable to a chemical reaction. The important
14 aqueous chemiluminescence substances luminal and lucigenin
15 were discovered in 1928 and 1935, respectively. A series of
16 organic soluble chemiluminescent materials were developed in
17 the early 1960's based on a study of the luminescent
18 reactions of a number of organic compounds. A typical
19 organic system useful for chemiluminescence was disclosed by
20 Bollyky et al., U.S. Patent No. 3,597,362 and claimed to
21 exhibit a quantum efficiency of about 23% compared with about
22 3% for the best known aqueous systems.

1 In its most basic form the two-component, liquid phase
2 oxalate ester chemical light system must comprise an "oxalate
3 component" comprising an oxalic acid ester and a solvent, and
4 a "peroxide component" comprising hydrogen peroxide and a
5 solvent or mixture of solvents. In addition, an efficient
6 fluorescer must be contained in one of the components. An
7 efficient catalyst, necessary for maximizing intensity and
8 lifetime control, may be contained in one of the components.

9 The oxalate component provides an oxalate ester-solvent
10 combination which permits suitable ester solubility and
11 storage stability. The peroxide component provides a
12 hydrogen peroxide-solvent combination which permits suitable
13 hydrogen peroxide solubility and storage stability.

14 The solvents of the two components may be different but
15 must be miscible. At least one solvent solubilizes the
16 efficient fluorescer and at least one of the solvents
17 solubilizes the efficient catalyst.

18 Typical suitable fluorescent compounds for use in the
19 present invention are those which have spectral emission
20 falling between about 300 and 1200 nanometers and which are
21 at least partially soluble in the diluent employed. Among
22 these are the conjugated polycyclic aromatic compounds having

1 at least 3 fused rings, such as : anthracene, substituted
2 anthracene, benzanthracene, substituted benzanthracene,
3 phenanthrene, substituted phenanthrene, naphthacene,
4 substituted naphthacene, naphthalene, substituted
5 naphthalene, pentacene, substituted pentacene, perylene,
6 substituted perylene, violanthrone, substituted violanthrone,
7 and the like. Typical substituents for all of these are
8 phenyl, alkyl ($C_1 - C_{16}$), chloro, bromo, cyano, alkoxy (C_1
9 $-C_{16}$), and other like substituents which do not interfere
10 with the light generating reaction contemplated herein.

11 The preferred fluorescers are 9,10-bis(phenylethynyl)
12 anthracene, 1-methoxy-9,10-bis(phenylethynyl) anthracene,
13 perylene, rubrene, mono and dichloro substituted 9,10-
14 bis(phenylethynyl) anthracene, 5, 12-bis(phenylethynyl)
15 tetracene, 9, 10-diphenyl anthracene, and 16, 17-
16 didecycloxyviolanthrone.

17 The term "peroxide component," as used herein, means a
18 solution of a hydrogen peroxide compound, a hydroperoxide
19 compound, or a peroxide compound in a suitable diluent.

20 The term "hydrogen peroxide compound" includes (1)
21 hydrogen peroxide and (2) hydrogen peroxide producing
22 compounds.

1 Hydrogen peroxide is the preferred hydroperoxide and may
2 be employed as a solution of hydrogen peroxide in a solvent
3 or as an anhydrous hydrogen peroxide compound such as sodium
4 perborate, sodium peroxide, and the like. Whenever hydrogen
5 peroxide is contemplated to be employed, any suitable
6 compound may be substituted which will produce hydrogen
7 peroxide. The hydrogen peroxide concentration in the
8 peroxide component may range from about 0.2M to about 15M.
9 Preferably, the concentration ranges from about 1M to about
10 2M.

11 The lifetime and intensity of the chemiluminescent light
12 emitted can be regulated by the use of certain regulators
13 such as:

14 1) by the addition of a catalyst which changes the
15 rate of reaction of hydroperoxide. Catalysts which
16 accomplish that objective include those described in M.L.
17 Bender, "Chem. Revs.," Vol. 60, p.53 (1960). Also, catalysts
18 which alter the rate of reaction or the rate of
19 chemiluminescence include, but are not limited to those
20 accelerators of U.S. Patent 3,775,366, and decelerators of
21 U.S. Patents 3,691,085 and 3,704,231, or

22 2) by the variation of hydroperoxide; wherein both the

1 type and concentration of hydroperoxide are critical for the
2 purposes of regulation.

3 Of those catalysts known to be useful, sodium salicylate
4 and various tetraalkylammonium salicylates have been most
5 widely used. Lithium carboxylic acid salts, especially
6 lithium salicylate, lithium 2-chlorobenzoate, and lithium 5-
7 t-butyl salicylate are excellent catalysts for low
8 temperature systems.

9 As outlined above, chemical light is produced by mixing
10 an oxalate ester and hydrogen peroxide together in the
11 presence of a catalyst and a fluorescer. Typically, the
12 oxalate ester and fluorescer are dissolved in one solvent.
13 The hydrogen peroxide and catalyst are dissolved in another.
14 The typical chemical light device is a polyethylene or
15 polypropylene container with the two liquids inside,
16 separated until light is needed, for example, by packaging
17 one of the liquids in a sealed glass vial and floating the
18 vial in the second liquid. Light is generated when the end
19 user flexes the plastic outer container, fracturing the glass
20 vial or alternatively by destroying the integrity of a
21 separating member, e.g. a diaphragm or membrane, in any
22 suitable manner thereby allowing the two liquids to mix.

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1 Chemical light devices are practically non-biodegradable
2 due to the plastic utilized in their construction.

3 Polyolefins will exist for hundreds of years in the normal
4 environment without losing a significant portion of their
5 physical properties. This fact has created problems and
6 concerns in all chemical light devices markets, but
7 especially in the military and commercial fishing markets.

8 Additionally, the liquids inside these devices are not
9 designed for general release into the environment. The
10 commercially practiced solvent systems are, in fact,
11 considered marine pollutants in many parts of the world.

12 Worldwide, over fifty million devices per year are
13 consumed between the military and commercial fishing markets.
14 This volume of consumption and the manner of the consumption
15 is creating a waste and waste disposal problem. The
16 permanence of the plastic container making up the chemical
17 light devices contributes to this waste and waste disposal
18 problem.

19 Military use of chemical light devices includes
20 providing basic light (illumination), safety marking, covert
21 marking, and as training aids. The uses often involve wide
22 dispersion of multiple chemical light devices over large

1 surface areas of land (many acres). After use, evidence of
2 the military's activities are left behind (the chemical light
3 devices) and will persist for decades or longer. Depending
4 on where the military exercise occurs, this may not be
5 allowed (example: USA or Europe). Military personnel are
6 required in these areas to attempt to collect all consumed
7 chemical light devices.

8 Commercial fishermen utilizing long lines to catch
9 swordfish and some species of tuna use chemical light devices
10 as lures or attractants. The long lines are significant in
11 length (often miles long) and deploy thousands of hooks
12 pendent from the long line. A chemical light device is
13 typically attached over each hook. Therefore, thousands of
14 chemical light devices are deployed with each long line.
15 This style of fishing typically occurs at night, with the
16 line deployed in late afternoon or early evening and
17 retrieved the next morning. The commercial fishermen are
18 encouraged to disconnect the chemical light devices and to
19 return them to shore for proper disposal. All will
20 disconnect the chemical light devices, but many do not return
21 them to shore for disposal. Instead, they throw the chemical
22 light devices overboard into the oceans. This has created a

1 significant problem on beaches in many parts of the world,
2 with literally thousands of plastic chemical light devices
3 washing up onto a beach with the tides and currents.

4 If it were possible to provide a chemiluminescent
5 product and chemical system which was inherently
6 biodegradable in its environment of use, such that said
7 device, inclusive of the chemiluminescent components, could
8 re-enter the environment within a reasonable interval after
9 its usefulness was at an end, then a long-felt need in the
10 art would be satisfied.

11
12 DESCRIPTION OF THE PRIOR ART

13 U.S. Patent No. 5,409,751 is directed toward a
14 degradable container formed from polylactic acid(s) alone or
15 in combination with other hydroxycarboxylic acids.

16 U.S. Patent 5,759,569 teaches a biodegradable article
17 manufactured from trans polymers, e.g. trans-1,4-
18 polyisoprene, optionally blended with other biodegradable
19 components, e.g. starch.

20 U.S. Patent 5,346,929 discloses a biodegradable plastic
21 including a synthetic polymer, a natural polymer and a
22 polymer attacking agent, and articles made therefrom.

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1 U.S. Patent 5,760,118 is directed towards end uses of
2 biodegradable polymers, e.g. their end-use in frequently
3 littered products such as drink containers, construction
4 materials and the like.

5 While the art demonstrates that biodegradable polymer
6 containers are known, per se, the references nevertheless
7 fail to teach or suggest a biodegradable chemiluminescent
8 device, wherein the container and possibly the
9 chemiluminescent agents are all readily biodegradable.

10

11 SUMMARY OF THE INVENTION

12 Chemiluminescent articles and methods for their
13 production and use have now been developed which yield
14 chemical light devices that do not create a waste or waste
15 disposal problem. These new devices are exemplified in two
16 major forms with certain variations:

17 1.Devices that disintegrate but do not biodegrade

18 2.Devices that disintegrate and substantially
19 biodegrade.

20 With reference to materials useful as containment
21 devices in the present invention, the following definitions
22 are relied upon:

1 "Disintegrates" is defined as a material which self
2 disintegrates so as to lose its physical form;

3 "Biodegradable" is defined as a material whose component
4 parts reenter the food chain within a reasonable period of
5 time;

6 "Reentering the food chain" means that the component can
7 be utilized as a raw material (food) by either plants or
8 bacteria.

9 Unlike "normal" plastics, which degrade very slowly,
10 degradable plastics are manufactured so as to exhibit an
11 accelerated rate of decomposition. This acceleration is
12 accomplished by either adding an additional component which
13 degrades easily, or by reducing the inherent non-degradable
14 characteristics of the particular plastic material. Plastics
15 that disintegrate into small parts have been developed and
16 marketed for years and are called biodegradable.

17 Starch/polyolefin yard waste bags are an example of this
18 technology. These bags disintegrate (lose coherent form)
19 when they become wet (the starch dissolves in water and frees
20 the bound polyolefin that gave the bag its physical strength
21 and other characteristics). This technology does eliminate
22 the disposal problem of the bag (which could present a hazard

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1 to small children and/or animals) by allowing the bag to lose
2 its form. However, a significant part of the bag (the
3 polyolefin) does not actually re-enter the food-chain.
4 Therefore, by the above definition, these bags are not truly
5 biodegradable. Photodegradable (UV degradable) polymers are
6 another example of plastic materials that disintegrate into
7 smaller parts but may not completely re-enter the food chain.
8 Examples of this technology are polymers formed by inserting
9 into the polymer chain irregularities that are subject to
10 degradation by UV light. Illustrative of these
11 irregularities are carbonyl groups (ketone carbonyl
12 copolymers or carbon monoxide copolymers) or metal salts.
13 Significant questions remain regarding the extent of
14 degradation of most photodegradable plastics, i.e. do these
15 degrade into non-plastic products or do they simply
16 disintegrate into smaller pieces of plastic.

17 True biodegradable plastics do exist. These materials
18 are consumed by microorganisms such as bacteria, fungi, or
19 algae. The microorganisms break down the polymer chain and
20 consume the material through several methods. The polymers
21 can be either hydrolysable or water soluble. Some common
22 biodegradable plastics are polyesters, polyhydroxybutyrates,

1 and vinyl polymers. Examples of biodegradable polymers are
2 listed in Table 1.

3 TABLE 1

4 Plastic Type	5 Name	6 Abbreviation	7 Description
8 Polyesters	Polyglycolic Acid	PGA	Hydrolyzable polyhydroxy acid
9	Polyactic Acid	PLA	Hydrolyzable polyhydroxy acid; polymers derived from fermenting crops and dairy products; compostable
10	Polycaprolactone	PCL	Hydrolyzable; low softening and melting points; compostable; long time to degrade
11	Polyhydroxybutyrates	PHB	Hydrolyzable; produced as storage material by microorganisms; possibly degrades in aerobic and anaerobic conditions; stiff; brittle; poor solvent resistance
12	Polyhydroxyvalerate	PHBV	Hydrolyzable copolymer; processed similar to PHB; contains a substance to increase degradability, melting point, and toughness
13	Vinyl Polyvinyl Alcohol	PVOH	Water soluble; dissolves during composting
14	Polyvinyl Acetate	PVAC	Water soluble; predecessor to PVOH
15	Polyenlketone	PEK	Water soluble; derived from PVOH; possibly degrades in aerobic and anaerobic conditions

1 Chemical light devices have now been produced which,
2 dependent upon the materials of construction, either
3 disintegrate (like the yard waste bag example above) or truly
4 disintegrate and biodegrade.

5 In a particularly preferred embodiment, a device is
6 provided which has the ability to both disintegrate and
7 completely biodegrade. This embodiment incorporates an
8 entirely new solvent/materials of construction system from
9 that which has been previously suggested or disclosed in the
10 prior art.

11 Generally, chemiluminescent light is produced by the
12 reaction of a catalyzed hydrogen peroxide solution with an
13 oxalate solution. The main component of the oxalate solution
14 is usually bis(6-carbopentoxo-2,4,5-trichlorophenyl)oxalate
15 (CPPO) which is mixed with dibutyl phthalate and a
16 fluorescent dye (e.g., 9, 10 bis (phenylethynyl)
17 anthracene) (BPEA). The hydrogen peroxide solution
18 ("activator") typically includes a major portion of hydrogen
19 peroxide, tertiary butanol, dimethyl phthalate and a catalyst
20 (e.g., salicylate of sodium or other metal).

21 This new biodegradable chemical light system includes

1 the following:

- 2 1. A liquid carrier capable of solubilizing the oxalate
3 ester and the fluorescer;
- 4 2. A liquid carrier capable of solubilizing the hydrogen
5 peroxide and catalyst;
6 wherein both liquids must be biodegradable; and
- 7 3. A plastic that is formable, flexible and biodegradable
8 wherein said plastic is compatible with both the liquids
9 and the chemical light active ingredients.

10
11 Accordingly, it is an objective of the instant invention
12 to provide an article of manufacture, in the form of a
13 chemiluminescent light producing device, which is completely
14 biodegradable.

15 It is another objective of the instant invention to
16 provide a container for retaining a chemiluminescent chemical
17 light system which is completely biodegradable.

18 It is a further objective of the instant invention to
19 provide a container for retaining a chemiluminescent chemical
20 light system which disintegrates but does not biodegrade.

21 It is yet another objective of the instant invention to

1 provide a container for retaining a chemiluminescent chemical
2 light system which disintegrates and substantially
3 biodegrades.

4 It is a still further objective of the instant invention
5 to provide a methodology for selecting/formulating the
6 constituents of a chemiluminescent chemical light system
7 which is biodegradable, and any chemiluminescent chemical
8 light system produced thereby.

9 Other objects and advantages of this invention will
10 become apparent from the following description, wherein are
11 set forth, by way of illustration and example, certain
12 embodiments of this invention.

13

14 DETAILED DESCRIPTION OF THE INVENTION

15 The present invention includes chemiluminescent light
16 producing devices, e.g. light sticks, wherein their materials
17 of construction enable them to be characterized as being
18 particularly susceptible to environmental degradation, and
19 which may be categorized as follows:

20

21

CONTAINER PROPERTIES	CHEMICAL SYSTEM PROPERTIES
Disintegrates/does not Biodegrade	Standard Chemical System/ Biodegradable Chemical System
Disintegrates/Partially Biodegrades	Standard Chemical System/ Biodegradable Chemical System
Disintegrates and Biodegrades	Standard Chemical System/ Biodegradable Chemical System

These systems are more properly illustrated by the following examples:

Example 1-*Device that disintegrates but does not biodegrade:*

Extrude into a tubular form a starch/polyolefin combination. Heat seal one end and fill with a typical chemical light oxalate solution (91.6% deputy phthalate, 8.4% CPPO, 0.19% BPEA). Float within the oxalate solution a sealed glass vial containing a typical chemical light activator solution (85% dimethyl phthalate, 10% t-butanol, 5% of 70% concentration hydrogen peroxide, 0.0085% sodium salicylate). Heat seal the remaining end. Flex to break the glass vial and light will result. Drop the device into water and it will soften and then dissolve. However, the polyolefin will remain and be unaffected over a long period of time (decades). Additionally, although not

1 environmentally hazardous in small quantities, e.g. that
2 found in a lightstick, the solvents, if released in large
3 quantities may present environmental and toxicological
4 problems as known marine pollutants (dibutyl phthalate) and
5 possible endocrine disruptors (dimethyl phthalate). Neither
6 has a particularly high bioavailability.

7
8 **Example 2-***Device that disintegrates and partially*
9 *biodegrades:*

10 Extrude into a tubular form a polyvinyl
11 alcohol/polyvinyl acetate combination. Heat seal one end and
12 fill with a typical chemical light oxalate solution (91.6%
13 dibutyl phthalate, 8.4% CPPO, 0.19% BPEA). Float within the
14 oxalate solution a sealed glass vial containing a typical
15 chemical light activator solution (85% dimethyl phthalate,
16 10% t-butanol, 5% of 70% concentration hydrogen peroxide,
17 0.0085% sodium salicylate). Heat seal the remaining end.
18 Flex to break the glass vial and light will result. Drop the
19 device into water and it will soften and then dissolve. With
20 the addition of normal soil bacteria, the polyvinyl
21 alcohol/polyvinyl acetate combination will be consumed (this

1 PVA combination has the same bioavailability as cellulose in
2 the normal environment). Although not environmentally
3 hazardous in small quantities, e.g. that found in a
4 lightstick, the solvents, if released in large quantities may
5 present environmental and toxicological problems as known
6 marine pollutants (dibutyl phthalate) and possible endocrine
7 disruptors (dimethyl phthalate). Neither has a particularly
8 high bioavailability.

9

10 **Example 3** -*Device that disintegrates and partially*
11 *biodegrades:*

12 Extrude into thin sheet form a ketone carbonyl copolymer
13 (vinyl ketone comonomer inserted into polyethylene).
14 Thermoform it into a shallow cup with a lip. Drop into the
15 cup a non-woven polyester felt pad or sheet and two sealed
16 glass vials, one containing a typical oxalate component
17 (91.6% dibutyl phthalate, 8.4% CPPPO, 0.19% BPEA) and the
18 other containing a typical activator component (85% dimethyl
19 phthalate, 10% t-butanol, 5% of 70% concentration hydrogen
20 peroxide, 0.0085% sodium salicylate). Heat seal a flat sheet
21 of the ketone carbonyl copolymer onto the cup lip, forming a

1 sealed container with the felt sheet and vials. Flex the
2 entire unit, breaking the glass vials and allowing the
3 liquids to mix and soak into the felt, creating light. Leave
4 the light device outside where it can and will be exposed to
5 sunlight (and in particular, UV light). The plastic
6 container will degrade and disintegrate. It may reenter the
7 food chain in a reasonable length of time. The felt sheet
8 and the solvents released will not degrade quickly and
9 present possible environmental and toxicological problems.

10
11 **Example 4** -*Device that disintegrates and biodegrades:*

12 Injection mold a tube and cap combination from a polyvinyl
13 alcohol/polyvinyl acetate combination. Contain within (prior
14 to sealing the tube and cap together) an oxalate component
15 made with 8.4% CPPO, 0.19% BPEA, and 91.41% of a 50/50
16 mixture of propylene glycol dibenzoate and acetyltributyl
17 citrate. Float within this oxalate component a sealed glass
18 vial containing 85% triethyl citrate, 10% t-butanol, 5% of
19 70% concentration hydrogen peroxide, and 0.0085% sodium
20 salicylate. Seal the cap and tube together and flex to break
21 the glass vial and allow mixing of the liquids. Light will

1 result. The expired device may be buried in the ground
2 (typical landfill disposal) or alternatively disposed of at
3 sea, or the like. Naturally occurring bacteria will consume
4 the polymer and the solvent combinations in a reasonable
5 period of time (both the polymer and solvents have a
6 bioavailability similar to cellulose).

7

8

9 Biodegradable chemiluminescent chemical light systems
10 are selected in accordance with the following criteria:

11

12 Oxalate Solvent Selection Rules:

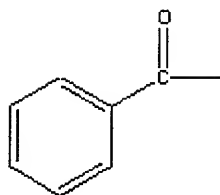
13 1. Select a general set of parameters or limiters that
14 you wish or need to meet, i.e. a particular biodegradable
15 characteristic such as comprising a biodegradable solvent
16 with a bioavailability close to that of cellulose.

17

18 2. Select a class of solvents that meets the
19 parameters set forth in Number 1.

20

1 3. Find members of this class of solvents that contain
2 a carboxy-phenyl group:



3

4 Solvents containing at least one carboxy-phenyl group
5 within their structure can and will solvate the active
6 chemical light ingredients (CPPO and fluorescers). Group the
7 members in order of water miscibility so as to optimize the
8 degree of CPPO solubility.

9 4. If the class of solvents does not contain any
10 members with a carboxy-phenyl group but is still the best
11 candidate to satisfy the parameters set forth in Number 1,
12 then choose a second class of solvents that comes close to
13 meeting the requirements of Number 1, is miscible in the
14 class of solvents chosen in Number 3, has at least one member
15 with a carboxy-phenyl group, and rank via water miscibility.

5. Make mixtures of the solvents chosen in Steps 3 and 4 with varying concentrations of each solvent. Blend into them different levels of CPPO and the individual fluorescers. CPPO solubility DECREASES with decreasing concentration of the solvent chosen in Step 4. The solvent chosen in Step 4 was deliberately chosen to optimize the degree of CPPO solubility of members of that group. The optimum combination of solvents, CPPO, and fluorescer will have to be determined empirically due to the differing absorption of the different colors of light by different solvents (a solvent that absorbs in the blue region of the spectrum will require a higher concentration of CPPO and blue fluorescer than a solvent that absorbs in the red end of the spectrum).

Activator Solvent Selection Rules:

1. Return to the class of solvents chosen in Step 2 of the Oxalate Selection Rules.

2. From this class of solvents, find all members that have a miscibility in water effective to stabilize the peroxide component of the chemical light activator system.

1 3. If no members of the class of solvents chosen in Step
2 2 of the Oxalate Selection Rules has a miscibility in to
3 effectively stabilize the peroxide component, then choose a
4 second class of solvents that comes close to meeting the
5 requirements of Number 1 from the Oxalate Selection Rules, is
6 miscible in the class of solvents chosen in Number 2 of the
7 Oxalate Selection Rules, and has member(s) that effectively
8 stabilize the peroxide component.

9 4. Make mixtures of the solvents chosen in Steps 2 and
10 3 with varying concentrations of each solvent. Choose the
11 blend that contains the highest concentration of the desired
12 solvent (that chosen in Step 2 of the Oxalate Selection
13 Rules) AND effectively stabilizes the peroxide component.

14 All patents and publications mentioned in this
15 specification are indicative of the levels of those skilled
16 in the art to which the invention pertains. All patents and
17 publications are herein incorporated by reference to the same
18 extent as if each individual publication was specifically and
19 individually indicated to be incorporated by reference.

1 It is to be understood that while a certain form of the
2 invention is illustrated, it is not to be limited to the
3 specific form or arrangement herein described and shown. It
4 will be apparent to those skilled in the art that various
5 changes may be made without departing from the scope of the
6 invention and the invention is not to be considered limited
7 to what is shown and described in the specification.

8 One skilled in the art will readily appreciate that the
9 present invention is well adapted to carry out the objectives
10 and obtain the ends and advantages mentioned, as well as
11 those inherent therein. The embodiments, methods, procedures
12 and techniques described herein are presently representative
13 of the preferred embodiments, are intended to be exemplary
14 and are not intended as limitations on the scope. Changes
15 therein and other uses will occur to those skilled in the art
16 which are encompassed within the spirit of the invention and
17 are defined by the scope of the appended claims. Although
18 the invention has been described in connection with specific
19 preferred embodiments, it should be understood that the
20 invention as claimed should not be unduly limited to such
21 specific embodiments. Indeed, various modifications of the

1 described modes for carrying out the invention which are
2 obvious to those skilled in the art are intended to be within
3 the scope of the following claims.

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